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Finite Size Effect on Drift Mobility and Diffusion Coefficient in Thin Organic Layers: Monte-Carlo and Analytic Modeling

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Abstract

Hopping transport of charge carriers in thin (< 100 nm) organic layers is modeled, using Gaussian disorder model. Monte-Carlo simulations yield considerable decrease of drift mobility with thickness of the layer, which is in good agreement with the developed analytic model. The reason is that filling of rare deep states is statistically improbable in course of transient across a thin sample. Quasi-equilibrium initial distribution is considered to omit effects of dispersive transport. Results of the work can explain disagreement in results of non-stationary and stationary measurements of transport coefficients in thin films.

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Keywords: mobilty; diffusion coefficient; finite size effect; disordered organic materials; Monte-Carlo simulations.

1. Introduction

Nowadays, devices of organic electronics are characterized by thin (10 – 100 nm) active layers. Charge transport can be described in the framework of Gaussian disorder model (GDM) by Bässler (1993). Variety of physical reasons can result in variation of transport coefficients with layer thickness – peculiarities of structure in near-surface region, effects of injection and non-equilibrium (NE) phenomena on transport. The latter effect is known as

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dispersive transport, which manifests itself in measurements of non-stationary processes according to Bässler (1993), Baranovskii (2014). Time-of-flight (TOF) measurements are, unfortunately, not applicable to thin layers.

In recent years, methods of non-stationary measurements in thin films, giving additional information on transport in respect to stationary (for example, I-V) measurements, such as impedance-spectroscopy, charge extraction by linearly increasing voltage (CELIV), and dark injection, have been developed intensively. Experimental results from various non-stationary methods show decrease of drift mobility with the increase of thickness of the layer. It can results from dispersive transport, but it can be also a manifestation of microscopic non-uniformity of disordered organic material. We focus on this effect in this paper. One has to expect, according to Nikitenko et al. (2011), that mobility and diffusion coefficient are size-dependent on a spatial scale of tens and even hundreds of nanometers (mobility), up to several micrometers (diffusion coefficient), in accord with Monte-Carlo (MC) simulations. The reason is that film thickness is less or comparable with the scale of network of pathways, which yields general contribution to transport in disordered media, see Baranovskii (2014). In other words, a carrier, passing through a thin film, has small probability to meet rather deep states, which control mobility and diffusion coefficient. These finite size ("mesoscopic") effects were found in MC and semianalytic calculations in 1D case by Baranovskii et al. (2001).

In this paper mobility and diffusion coefficient of charge carriers in 3D case are analysed by the joint analytic and MC modelling at various values of film thickness, temperature and electric field strength. It shows that both temperature dependence and absolute values of drift mobility differ considerably from well-known results by Bässler (1993) for infinite media. Results of the analytic model are in good agreement with MC modelling.

2. Model of Monte-Carlo simulations

We use a conventional model by Bässler (1993), where hopping centres are located at sites of simple cubic lattice with a lattice constant a_0. Energies of sites are distributed randomly according to Gaussian distribution, $g(E)$.

Hopping rate from site i to site j, of energies E_i and E_j, respectively, is determined by Miller-Abrahams (MA) expression, providing that constant electric field F is on: $\nu_{ij} = \omega_0 \exp\left| -2\gamma r - (\Delta E_{ij} + \left|\Delta E_{ij}\right|)/2kT \right|$, where ω_0 is the frequency factor, γ is the inverse radius of localization, r is the distance between two sites, $\Delta E_{ij} = E_i - E_j - eFr\cos\theta$, T is the absolute temperature, k is the Boltzmann constant, and θ is the angle between vector of electric field $\boldsymbol{F}$ and jump vector $\boldsymbol{r}$. The value of $2\gamma a_0 = 10$ is assumed. Energetic distribution of generated carriers is taken to be quasi-equilibrium (QE) in order to omit effects of dispersive transport, providing low-concentration limit, $g_{occ}(E) \propto g(E) \exp(-E/kT)$. Number of sites along any transversal direction exceeds 10 times number of sites, N, along the electric field direction.

Procedure of simulations includes 10 000 events of passage of a carrier from the place of its birth to the right boundary of a sample, see more detailed description of method by Nikitanko et al. (2014). Mobility of charged particles is calculated by the average drift velocity, i.e. by an average (over 10 000 events) inverse transit time t_{tr} according to Nikitenko et al. (2011) and Baranovskii et al. (2001), $\mu = L/F \langle 1/t_{tr} \rangle$. A carrier can move within l layers to the left from the first layer, where an electron being born. Number l satisfies the condition: $leFa_0/kT >> 1$, hence visit of a carrier the real left boundary is improbable. It allows analyzing the mobility, depending on the medium properties, without influence of the electrode (dummy injecting electrode).

Calculation of the mobility via $\langle 1/t_{tr} \rangle$ (not via $1/\langle t_{tr} \rangle$) better corresponds to definition of the product μF as the average drift velocity. Values of $\langle 1/t_{tr} \rangle$ and $1/\langle t_{tr} \rangle$ become equal to each other in the limit of thick films ($L > 1$ mcm). Calculation via the average transit time, $\mu = \mu_t = L / (F \langle t_{tr} \rangle)$, is transparent from the point of view of TOF experiments. But this way of calculation overestimates contribution of "slow" carriers to the drift mobility. Averaging of transit times is correct for thick layers, where pathways of carriers unavoidably include deep states with long release times ("slow" states), while averaging of *inverse* transit times clarify the finite-size effect in a thin layer, where finite chains of "fast" states, being in parallel to each other, can have influence on conductivity, see the work by Baranovskii et al. (2001). The condition $eFL/kT >> 1$, that provides neglect of diffusion current, is well satisfied in these calculations.

3. Analytic model

The basic idea of the analytic model is the following: probability to meet a deep state, which determines drift mobility and diffusion coefficient, decreases along with the number of states N_0, visited by carrier. Average (over the ensemble of drifting carriers) value $\langle N_0 \rangle$, obviously, decreases along with decreasing of film thickness or with increasing of field strength. The simplest approach is to "cut off" deep states ($E < E_*$) from the Gaussian density of states (DOS), hence to introduce the effective DOS $g_{eff}(E)$:

$$g_{eff}(E) = g(E), \quad E \geq E_*; \quad g_{eff}(E) = 0, \quad E < E_*, \tag{1}$$

where the "cut-off" energy E_* is determined by the condition, that the average number of captions by states with energies $E < E_*$, as a carrier passes through the layer, is equal to unity:

$$\langle N \rangle = \langle N_0 \rangle \varphi(E_*) = 1, \tag{2}$$

where $\varphi(E)$ is the probability of carrier's capture to a state of energy $E' < E$ after each hop. $\langle N \rangle(E) < 1$, if $E < E_*$, hence capture to these states is unlikely. Number of visited sites within the layer can be estimated as follows: $\langle N_0 \rangle = t_{tr} \langle 1/t_1 \rangle$, where $\langle 1/t_1 \rangle$ is average inverse time of a single hop. By the definition, $t_{tr} = L/\mu F$, where μ is the drift mobility, value of $\langle 1/t_1 \rangle$ can be estimated from the values of the usual, not field-stimulated diffusion coefficient: $\langle 1/t_1 \rangle \approx D_0/a^2$, a is the typical hopping length. Thus, the expression of $\langle N_0 \rangle$, contains ratio D_0/μ, which is estimated by Einstein relation, $D_0/\mu = kT/e$. The probability $\varphi(E)$ in Eq. (2) is calculated as follows:

$$\varphi(E) = \int_{-\infty}^{\infty} dE_i \Phi(E_i) \tilde{\varphi}(E, E_i), \tag{3}$$

where $\tilde{\varphi}(E, E_i)$ is the probability that the carrier gets a state with energy which is not above E, providing a hop from a state with energy E_i. $\Phi(E_i)$ is normalized probability density to make the hop from a state with energy E_i,

$$\Phi(E_i) = g_{occ}(E_i) \omega(E_i) \Big/ \int_{-\infty}^{\infty} dE' g_{occ}(E') \omega(E'), \tag{4}$$

where $g_{occ}(E) = g(E) \exp(-E/kT) \Big/ \int_{-\infty}^{\infty} dE' g(E') \exp(-E'/kT)$ is the distribution of occupied states (in the QE low-concentration model), see the work by Nikitenko and Strikhanov (2014). The typical rate of hops from a state of energy E, $\omega(E)$, is calculated according to the MA model, $\omega(E) = \nu_0 \exp[-u(E_{trans} - E)]$, where $u(x) \equiv (x + |x|)/2kT$ and E_{trans} – the transport level (TL) described in detail by Nikitenko and Strikhanov (2014). E_{trans} is introduced as an upper level of states, releasing carriers by upward (in energy) jumps predominantly. This statement is confirmed by the recent MC simulations by Arkhipov and Rudenko (1982). Similarly, we define a function $\tilde{\varphi}(E, E_i)$,

$$\tilde{\varphi}(E, E_i) = \int_{-\infty}^{E} dE' g(E') \exp[-u(E' - E_i)] \Big/ \int_{-\infty}^{\infty} dE'' g(E'') \exp[-u(E'' - E_i)]. \tag{5}$$

Using (3)-(5), we can write Eq. (2) as follows:

$$\frac{LkT}{eFa^2} \int_{-\infty}^{E_*} dE g(E) \Psi(E) = 1, \tag{6}$$

where in realistic case of $E_* < E_{trans}$

$$\Psi(E) = \tilde{I}^{-1} \left(\int_{-\infty}^{E} dE_i g(E_i) I^{-1}(E_i) \exp\left[-u(E - E_i) - \frac{E_{trans}}{kT} \right] + \int_{E_{trans}}^{\infty} dE_i g(E_i) I^{-1}(E_i) \exp\left(-\frac{E_i}{kT} \right) \right), \tag{7}$$

where $\tilde{I}(E_{trans}) = \int_{-\infty}^{\infty} dE g(E) \exp[-E/kT - u(E_{trans} - E)]$, $I(E_i) = \int_{-\infty}^{\infty} dE g(E) \exp[-u(E' - E_i)]$. If $E << E_{trans}$, so that

energetically down hops predominates, then equations (6), (7) are significantly simplified, since $\Psi(E) \approx \Psi_\infty$,

$$\Psi_\infty = \tilde{I}^{-1} \int_{-\infty}^{\infty} dE_i g(E_i) I^{-1}(E_i) \exp\left[-u(E_{trans} - E_i) - \frac{E_i}{kT} \right]. \quad (8)$$

The "cut-off" energy, E_*, decreases along with increasing of a layer thickness. If E_* exceeds the average energy of QE distribution of occupied states, $-\sigma^2/kT$, which determines the magnitude of infinite-medium mobility, see the works by Bässler (1993), Baranovskii (2014), mobility considerably exceeds this magnitude, and mobility decreases, if a layer thickness increases. Field-stimulated diffusion coefficient is determined by scatter of the occupation times of the carrier in deeper states, about $-2\sigma^2/kT$, according to Bässler et al. (2007). Decrease of the number of states, visited by the carrier, decreases the probability of capture at such deep states. This fact leads to the increase of field stimulated diffusion coefficient with increasing layer thickness in the thickness range, which is much wider than the range of thickness at which mobility decreases, and the values of this coefficient are much smaller than predicted for the infinite medium.

The mobility and the diffusion coefficient are calculated using equations similar to the equations of the multiple trapping model, see Bässler et al. (2007), Nikitenko and Strikhanov (2014), with replacing the Gaussian function by $g_{eff}(E, L, F)$, see Eq. (1),

$$\mu = \mu_0 \nu_0 \tau_0 \Big/ \int_{E_*(L,F)}^{E_{trans}} dE\, g(E) \exp\left[(E_{trans} - E)/kT \right] \quad (9)$$

$$D = D_0 + \mu^2 F^2 \langle t_{rel} \rangle, \quad D_0 = \mu kT/e, \quad (10)$$

$$\langle t_{rel} \rangle = \nu_0^{-1} \int_{E_*(L,F)}^{E_{trans}} dE g_{occ}(E) \exp\left[(E_{trans} - E)/kT \right], \quad (11)$$

where $\mu_0 = \nu_0 (e/kT)(a^2/6)$ is a mobility at "conducting" states (near TL), $\nu_0 = \omega_0 \exp(-2\gamma a)$ is characteristic rate of tunnelling jumps between "conducting" states, τ_0 is lifetime of carriers at "conducting" states. Previous analysis by Nikitenko and Strikhanov (2014) yielded $\tau_0 \nu_0 \approx kT/\sigma$.

4. Results and discussion

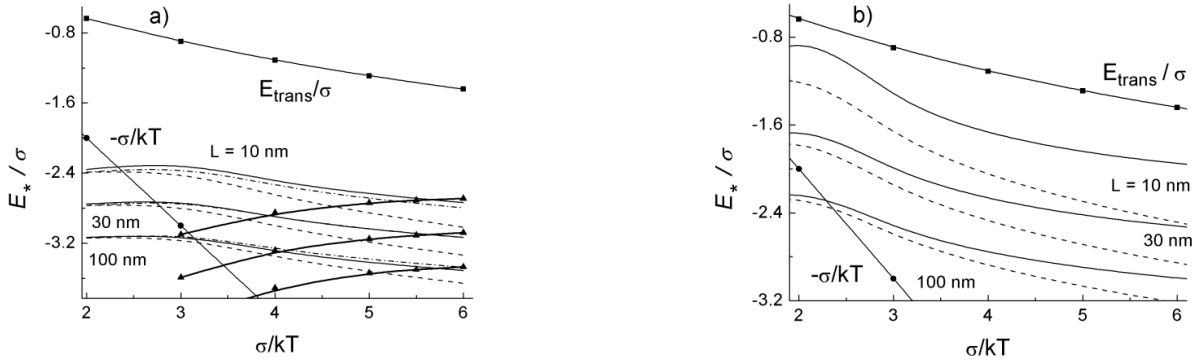

Fig. 1. Normalized "cut-off" energy at electric field strength $F = 1 \cdot 10^5$ *V/cm* (a) and $F = 5 \cdot 10^5$ V/cm (b), solid lines. Dashed and dash-dotted lines – approximations by Eq. (12), see text. Here and below $2\gamma N_t^{-1/3} = 10$, $T = 300$ *K*, $a_0 = N_t^{-1/3} = 1$ nm, where N_t – spatial density of states. Normalized TL (lines with squares), mean energy of QE distribution of charge carriers (line with circles) and demarcation energy $E_d(t_{tr})$ at the moment of transit time for various thicknesses (lines with triangles), see Eq. (16), are also shown.

Normalized "cut-off" energy, E_*, is calculated from Eq. (6) and is shown in Fig. 1, parametric in film thickness, *L*. Normalized mean energy of occupied states, $-\sigma^2/kT$, and TL, E_{trans}, are also shown in Fig. 1 by lines with symbols. Obviously, the energy E_* decreases with the increase of σ/kT slower, than the mean energy, $-\sigma^2/kT$,

hence "cut-off" of the DOS effects on mobility in strong disorder case. The condition of applicability of Eq. (6), $E_* << E_{trans}$, is fulfilled, especially at low field strength. One can simplify Eq. (6), if $\Psi(E) = const \equiv \Psi_\infty$:

$$\int_{-\infty}^{E_*} dEg(E) = eFa^2 / (\Psi_\infty LkT). \quad (12)$$

Calculating of Ψ_∞ from Eq. (8), however, yields quantitative disagreement in strong disorder case, see dashed lines in Fig. 1. One can achieve quantitative fit at low field strength, providing that $\Psi_\infty = \exp\left(b\hat{\sigma} - c\hat{\sigma}^2\right)$, $2 < \hat{\sigma} < 6$, $\hat{\sigma} = \sigma/kT$, $b = 0.80$, $c = 0.04$, see dash-dotted lines in Fig. 1a.

The results of MC simulations and analytic modelling of drift mobility in thin (20 – 100 nm) organic layers are shown in Fig. 2. Analytic model yields quantitatively accurate fit of MC results at weak field, $F = 1 \cdot 10^5$ V/cm, while at strong field agreement is only qualitative. The possible reason is small depth of the "cut-off" energy relative to TL at small values of L, see Fig. 1b. Dependence of drift mobility on film thickness follows power law with the exponent $\beta \cong 1$, see Nikitenko et al. (2011),

$$\mu(L) = \mu_\infty \left[1 + (L/L_0)^{-\beta}\right], \quad (13)$$

where L is the characteristic length ($\mu/\mu_\infty < 2$, if $L > L_0$). For example, for $F = 1 \cdot 10^5$ V/cm values of $\mu_\infty/\mu_C = 0.101$, 0.012 and 0.00090; $L/a_0 = 9.5$, 20.9 and 57.4; $\beta = 1.14$, 1.0, 1.03 for $\sigma/kT = 2$, 3 and 4, respectively. Obviously, decrease of mobility along with increase of disorder becomes progressively slower, if thickness decreases. Low-disorder slope of infinite-medium mobility, μ_∞, see line 1 in Fig. 2a, follows the well-known law by Bässler (1993),

$$\mu_\infty = \mu_C \exp\left[-C(\sigma/kT)^2\right], \quad (14)$$

where $C = 0.43$ at $2\gamma a_0 = 10$ is in good agreement with well-known MC and analytic (the TL concept) results by Bässler (1993) and Baranovskii (2014), respectively. Deviations from the law (14) at strong disorder ($\sigma \geq 4$), probably, related to NE initial population of finite system of hopping centers, which is unavoidable at high disorder according to Lukyanov and Andrienko (2010). This circumstance causes deviation of the infinite-medium extrapolation, μ_∞, from the law (14). This deviation is not sufficient, however, at $\sigma/kT \leq 4$, see dashed line in Fig. 2b, while finite-size effect dominates the deviation of drift mobility from the law (14). At $L = 100$, 50 and 20 nm, one obtains $C = 0.40$, 0.38 and 0.35, respectively, in low-disorder limit. Disorder dependence progressively approaches to Arrhenius-type function along with the decrease of thickness, see Fig. 2b, reminiscent to dispersive transport, see the work by Baranovskii (2014). Qualitatively, finite-size effect is similar to dispersive transport. In both cases, NE energetic distribution of charge carriers approaches to QE in course of transport. In the former case, initial QE is violated at initial time interval, because "fast" carriers cannot find states with energies $E < E_*$ during

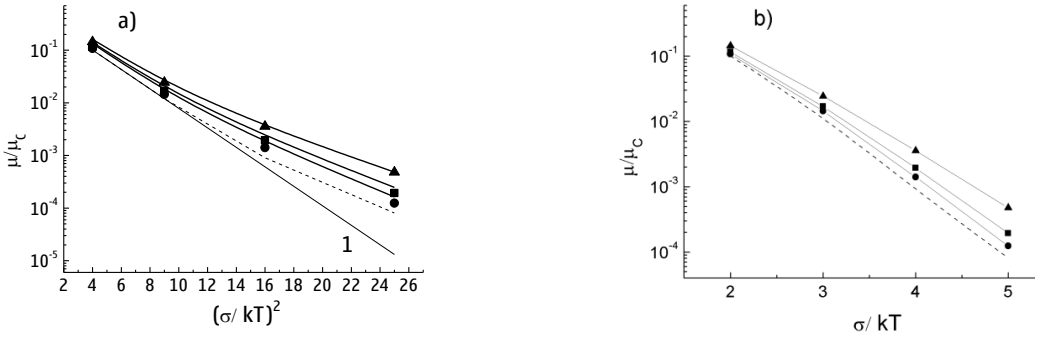

Fig. 2. Dependence of drift mobility on disorder parameter, σ/kT. Triangles, squares and circles show MC-results at L = 20, 50 and 100 nm, respectively, solid lines – analytic results at the same thicknesses, dashed line – infinite-medium limit of mobility, μ_∞. Line 1 shows the law (14) with C = 0.43.

their passage across the sample. In the latter case, QE is absent initially. Dispersive transport is characterized by time-dependent demarcation energy, $E_d(t) = E_{trans} - kT \ln(\nu_0 t)$, $\nu_0 t >> 1$, ($t = 0$ is the moment of generation), see Bässler et al. (2007). Shallow states, $E > E_d(t)$, are in quasi-equilibrium, while deep states, $E > E_d(t)$, remain far from equilibrium population, hence $E_d(t)$ is the maximum of distribution of occupied states, providing that $E_d(t) > -\sigma^2/kT$, and conventional dispersive transport occurs. However, states around $E_d(t)$ are not populated, if $E_* > E_d(t)$. In this case, finite-size effect dominates kinetics of charge carriers. Fig. 1a) shows dependences of $E_d(t_{tr})$ on σ/kT, calculated at various thicknesses L as follows:

$$E_d\left(t_{tr}\right) = E_{trans} - kT \ln\left[\nu_0 L / \mu(L) F\right], \tag{15}$$

where drift mobility $\mu(L)$ is determined by Eq. (13). Apparently, finite-size effect dominates charge transport at moderate disorder and rather small thickness of the sample; hence coincidence of results for QE and NE generation of charge carriers is not surprising. One can easy estimate a thickness dependence of mobility in case of dispersive transport by usual equation, $\mu(L) = L / F\, t_{tr}(L)$. On base of the TL concept and results of the multiple-trapping model, Bässler et al. (2007), Arkhipov and Rudenko (1982), transit time in dispersive regime results from equation $\langle x(t_{tr})\rangle = \mu_0 F \tau(t_{tr}) = L$. One can write the function $\tau(t_{tr})$ in a power-law form, $\tau(t) \propto t^{\alpha(t)}$, $\alpha(t) = 2(\sigma/kT)^2 / \ln(\nu_0 t)$, at reasonable condition $|E_d(t)|/\sigma >> 1$. Eventually, one obtains formally a power-law, $\mu_{disp}(L) \propto L^{-\beta_{disp}}$, where the exponent, $\beta_{disp} = |2(\sigma/kT)^2 / \ln(\nu_0 t_{tr}(L, F))| - 1$, depends on transit time (consequently, on thickness and field strength), in contrast with the "finite size" exponent β. In dispersive regime, $\nu_0 t_{tr} < \exp|(\sigma/kT)^2)|$, according to Baranovskii (2014), hence $\beta_{disp} > 1$. For example, at $\sigma/kT = 4$ the value of β_{disp} decreases from 2.4 to 1.7 along with the increase of L from 20 to 100 nm at $F = 1 \cdot 10^5$ V/cm and from 3.9 to 2.4 at $F = 1 \cdot 10^5$ V/cm. Thus, one can distinguish, in principle, mesoscopic effect from conventional dispersive transport, which is caused by relaxation of initial NE energetic distribution. The parametric region, in which finite size effect prevails and has effect on mobility, is clear from Fig. 1a.

5. Conclusion

In this paper, an analytic model of finite size effect on transport coefficients under conditions of transient (non-stationary) measurements is developed, and it is in good agreement with MC modeling. Effective distribution of states with thickness-dependent minimal energy introduces. Qualitatively, manifestations of finite size effect are similar to dispersive transport, but the former could be distinguished from dispersive transport on base of the law of thickness- (or time-) dependence of mobility. In contrast with dispersive transport, finite size effect exists even at QE initial energetic distribution of charge carriers. This circumstance is important in analysis of non-stationary experimental results, as well as in modeling of properties of materials, basing on small boxes.

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